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BIOTREATMENT OF CLAYEY MATERIALS AND CERAMIC PASTES: DIRECTIONS, METHODS AND EXPERIENCE (REVIEW)

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Research on biological action on clayey materials and ceramic pastes is reviewed. The main directions and differences in biotreatment technology depending on the type of microorganisms, method of production and composition of the culture liquid, conditions and method of biotreatment, material composition and naturally occurring cenosis of clayey materials are determined. The role of the individual components of a culture liquid in changing biological and biochemical processes is shown. The experience gained in biotreatment applications in the ceramic industry is examined.

Key words: clayey materials, ceramic paste, maturing, biotreatment, cenosis, inoculum, culture liquid, nutrient medium, microorganisms.

Biotreatment is one of the methods used to improve the technological properties of clayey materials and ceramic pastes and to remove impurities, including colorants. Previously, the transformation of clayey materials was attributed solely to abiotic processes in a dispersion medium during technological processing: change of pH and redox state Eh, moisture, temperature, chemical composition of the dispersion medium and other changes. The main operations in the technological processing of clayey materials and clayey ceramic pastes (CCP) are conducted in an aqueous medium. Water also participates in biogenic processes. It is now clear that many processes leading to a change of the dispersion phase — disaggregation of particles, disordering of the structure, dissolution and synthesis of new minerals, formation of colloids — occur in the presence of microorganisms. Microorganisms living in silicate and aluminum-silicate rocks produce a number of metabolites and taken as a whole possess a high biotechnological and oxidation-reduction potential. It has been shown in many studies that the abiotic and biotic processes leading to transformation of clayey materials are similar; if bacteria participate in a process, then all processes resulting in the transformation of CCP are accelerated [1].

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At the present time, despite numerous experimental works, researchers are faced with more questions than there are answers. What types of microorganisms participate in the transformation of minerals? What is the nutrient and energy nature of these processes? What metabolites participate in these processes and how do they do so? Which processes play a positive and which a negative role in the biotreatment of ceramic pastes? There are many others.

All questions shedding light on the nature of the relationship between abiotic and biotic processes and the contribution of these processes to the improvement of the properties of CCP become important for theoretical work and practical applications.

The objective of the present review is to generalize the existing information on biotreatment technology and to determine the principal directions and methods of the biotreatment of clayey materials and ceramic pastes.

Principal Applications of Microorganisms. Different approaches to utilizing microorganisms to improve the quality of CCP are followed. The first, and conventional, approach is to allow CCP to mature under definite conditions and regimes; the second is to add to CCP chemical substances which promote the development of naturally occurring microflora or to introduce artificially bacterial cenosis or culture liquid for bacteria of a definite type.

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In general, the numerous studies and experimental-industrial projects on the biotreatment of CCP reduce to two problems:

1) action on the ceramic and rheological properties of pastes and casting slip based on clayey materials;

2) removal of impurities, predominately colorants and iron-containing, from CCP.

A number of conditions are used to regulating the maturing of CCP: the temperature of the ambient medium and the periodicity of its variation (procedure for combining abiotic and biotic processes, called "wintering-summering"), moisture, composition of organic and inorganic compounds in the dispersion medium, presence of naturally occurring microflora, and others. The direction and contribution of the physical-chemical, biochemical and biological processes leading to the modification of the components of ceramic paste depend on the maturing time and a combination of the factors enumerated above. It is noted in [2] that maturing in dark and warm enclosures for 6 – 10 days improves the molding properties of paste and increases the strength of the dried intermediate product.

A number physical-chemical processes occur as CCP matures: more complete development of hydrate films and adsorbed complexes around particles of the paste, first and foremost, clayey particles; increase of the colloidal fraction of the solid phase; and, formation of a denser paste structure. The change of the solid phase of CCP during maturing was also explained by the action of microorganisms and their metabolites. At least three processes occur as a result of the activity of the microorganisms in CCP: transformation of phase contacts between cemented particles and microaggregates into coagulation contacts; dispersion of mineral particles, structural disordering of the minerals and their dissolution with the colloid fraction increasing; and, synthesis of new biogenic minerals [3]. Thus, aside from the physical-chemical factors influencing the properties of CCP, biochemical and biological factors play an important role during maturing.

At the end of the 19th and beginning of the 20th centuries different methods were used in ceramic production to make CCP maturing more efficient by adding various substances. A number of publications reported on the use of various additives, including humic substances, dextrin, sugar syrup, chicken manure solution, metabolites from various domestic animals, and so forth, adding which gave positive results at ceramic enterprises in Russia [4, 5]. This method of increasing the maturing efficiency was known as "decay" [4]. The Chinese kept porcelain stones and clay in holes under water and poured liquid manure and urea on them [6].

Many studies of the nature and mechanism of the action of microflora as well as the development of technological processes for biotreatment of CCP were performed in the 20th century [1, 7, 8]. Decomposition, synthesis and recrystallization of many minerals as a result of the activity of microorganisms are much more prevalent than believed until recently [1, 8]. Examples of such interactions are presented in [1, 9], where an extensive bibliography can be found.

One successful application of microorganisms for enriching mineral raw material and improving the properties of CCP entails the use of *Bacillus mucilaginosus*, identified and described by V. G. Aleksandrov et al. [10]. These researchers named these organisms "silicate bacteria," by which name they were known for some time. The taxonomic position of *Bacillus mucilaginosus* remains unknown to this day [11].

A number of strains of bacteria close to the culture described by V. G. Aleksandrov were isolated in the course of a study of the microflora in rocks. The researchers assumed that the silicate bacteria are capable of, at the very least, utilizing the chemical-bond energy of clayey materials. In other words, silicate bacteria can "feed" on clays. However, this opinion is not confirmed experimentally. The authors of [11, 12] showed that this organism is heterotrophic and is incapable of growing without organic substrates. The activity in breaking down silicate minerals inheres in different microorganisms, though it should be noted that *Bacillus mucilaginosus* exhibits elevated activity in breaking the siloxane bond; this is due to the specific action of exopolysaccharides formed by this culture [3, 11].

The first studies of the utilization of *Bacillus mucilaginosus* nutrient medium for treatment of CCP were performed by Professor A. S. Vlasov et al. in the 1980s [13 – 15] and Professor G. N. Maslennikova et al. starting in the 1990s [3, 16, 17]. The biochemical and biological nature of the processes involved in the maturing of CCP under the action of the naturally occurring microflora and its metabolites were studied. It was shown in [16] that the following conditions are necessary during maturing: moisture, organic substances, naturally occurring or introduced microflora, and optimal temperature.

The studies of the effect of the *Bacillus mucilaginosus* nutrient medium on the metabolites formed and the rheological properties of CCP were continued in the Republic of Belarus [18].

Studies of the processes resulting in the removal of iron from CCP have been performed in the last few decades [16, 17, 19 – 27]. The iron present in weakly magnetic and amorphous (hydr)oxides and the "structural" iron of clayey materials can be removed only by chemical or biological methods [23]. Two methods are used to remove iron. These methods include different biological and biochemical processes. In the first variant, additions of the nutrient medium of bacteria, for example, *Bacillus cereus* [23] or fungi *Aspergillus niger* [24, 25], which produce organic acids capable of dissolving (hydr)oxides and complexation with the participation of iron compounds, are used. In the second variant, a nutrient medium, which contains different sources of carbon and nitrogen and promotes the development of the trophic chain of a microbial community, of which iron-reducing bacteria performed the main function, is introduced into the CCP [16, 19, 21, 26, 27].

Biotreatment Technology for Clayey Materials and Ceramic Pastes. The results of the studies of the biotreatment of CCP show that the action of the microorganisms and

the products of their activity exhibit differences as well as many similarities. The differences depend on, first and foremost, the following:

– use of different collections of bacterial strains, differing by origin and method of culturing and therefore activity during biotreatment;

– methods for obtaining live bacterial cells on different nutrients (nutrient medium), affecting the number of live cells formed (titer introduced) and the composition of the exometabolites;

– composition of the natural cenosis (community) of microorganisms in the clayey materials;

– biotreatment conditions: temperature, moisture and periodicity of changes in the moisture content (stagnant, stagnant wash), time, aeration as well as the amount and composition of the nutrient medium used in biotreatment;

– material composition of clayey materials;

– method of activation of the CCP.

Preparation of Active Strains of Bacteria. The production and utilization of high-activity strains of bacteria effectuating the required biological and biochemical processes are the most important factors determining the intensification of the biotreatment of CCP. The results of a series of studies of the production of high-activity strains of *Bacillus mucilaginosus* are examples [28]. The selective dissolution of silicate minerals using 10 naturally occurring strains separated from rocks and eight mutant strains obtained in the laboratory by exposure to x-rays and chemical compounds was studied. The best results were obtained with either rock-adapted mutant strains or a mixed population consisting of naturally occurring strains. Interesting results were obtained while analyzing two types of clay treated with *Bacillus circulans*. It was determined that pre-adaption to clay is a necessary condition for some bacterial strains and immaterial for others. Ultimately, the best results on breaking down minerals were obtained in variants maximizing biomass development. An evaluation of the development of *Bacillus mucilaginosus* using standard nutrient media showed that bacterial cells developed most intensively in porcelain paste with added molasses [15].

Naturally occurring cenosis of microorganisms in clayey materials. Recently, it was recognized that the largest population of microorganisms develops in clayey formations comprising unique regions inhabited by microorganisms. Most microorganisms are larger than clayey particles, and it is assumed that a population of microorganisms is found in clays in cases where they are captured in traps at the time the clayey layers were deposited. Analysis of quantitative accounting of different physiological groups of microorganisms for kaolin from the Prosyanovskoe deposit (Ukraine) revealed the dominant forms of bacteria: aerobic and facultative anaerobic are represented by *Bacillus sp.*, *Pseudomonas sp.* and *Arthobacter sp.*; *Bacillus sp.* and *Clostridium sp.* predominated among fermentative strains; the dominant form of sulfate-reducing bacteria is *Desulfovibro sp.*; and, the dominant iron-reducing bacteria is *Fe Red* [20]. Studies of kaolin samples of different age from the Georgia deposit (USA) also showed the presence of different physiological groups of microorganisms, such as fermentative, sulfate-reducing, methane-producing, and dissimulator Fe(III) — reducing microorganisms [21]. Therefore, the development and growth of natural microflora in CCP must be taken into account when a nutrient medium or culture liquid of bacteria is introduced.

*Material composition of CCP***.** The material composition of CCP consists mainly of clayey minerals, quartz, mica, iron and other minerals as well as an x-ray amorphous component and organic compounds. The material composition of clayey materials reflects the action of different abiotic and biotic processes involved in weathering of crust. In consequence, minerals are distinguished according to the degree of structural ordering, particle size, and specific surface area of particles as well as the type and number of interparticle contacts, which determine the sizes of aggregates, the microstructure and in aggregate the rheological properties of CCP. In an aqueous medium, condensation contacts can transform into coagulation contacts in contrast to phase contacts, strongly binding particles into microaggregates. Phase contacts are conventionally distinguished by composition as silica alumina gel and ferruginous, which fracture under different physical-chemical conditions.

Abiotic breakdown of clayey minerals occurs in a differential manner according to their thermodynamic stability. The thermodynamic stability of minerals does not play such a large role in biotic processes. Abiotic breakdown of minerals differs from biological and biochemical breakdown mainly by the attainment method and the mechanism of such reactions [29]. Biological breakdown of silicate minerals depends on their type, crystal-chemical particulars and specific surface area as well as on the nature of the microorganisms and their metabolites acting on them.

The mechanism by which Fe(III) containing minerals dissolve in a reducing medium created by a cenosis of microorganisms will differ from abiogenic dissolution of minerals. In general, Fe(III) is the main inorganic electron acceptor present in iron minerals and silicate minerals [29]. Intense reduction of Fe(III) in a lattice of silicates results in their breakdown. According to Roden's scheme [30], sorption of Fe(II) on the surface of minerals and subsequent retardation of Fe(III) reduction occur in stagnant bedding. Under these conditions biological reduction affects predominantly amorphous iron compounds. It is well known that amorphous iron compounds often appear in the role of a cementing phase between clayey minerals, creating strong dense aggregates. Disaggregation of CCP particles occurs in the presence of Fe(III) reduction in amorphous compounds and during their subsequent dissolution.

Conditions of Biotreatment. Microorganisms and their metabolites act on ceramic pastes when the moisture content is 50 – 60% at temperature 25 – 35°C.

The main stage of the biotreatment process is aeration. During continual mixing ceramic paste becomes enriched with oxygen and aerobic bacteria exhibit the greatest activity.

The duration of the biotreatment stage depends on the problem addressed by biotreatment. When pastes mature over a long time in storage aerobic microorganisms develop on the surface of the particles in the paste (maximum thickness to 5 – 10 mm). Inside CCP cakes, as microorganisms develop the dissolved oxygen is consumed in oxidation of organic substances, so that the redox potential decreases. An oxygen deficit impedes the activity of aerobic bacteria, so that anaerobic bacteria begin to develop. Gley formation develops when definite factors combine together [17]. If additional nutrients are not introduced, the maximum biotreatment time is 30 years; this is related with a decrease of the activity of bacteria in ceramic paste.

Two water regimes are used in biotreatment of CCP: stagnant — moisture content maintained for a definite period of time; stagnant wash — the liquid phase gradually seeps through the paste volume and carries out the soluble compounds which are formed. The first regime occurs during maturing of CCP; the second one occurs during maturing on open areas or is produced by using specialized equipment.

Repeated biotreatment of casting slip prepared from biotreated paste or containing electrolytes is less effective. This is related with the replacement of active centers of clayey particles by products of bacterial activity and cations introduced with the electrolytes as clayey pastes are thinned [15].

Bioactivation methods. Several methods of bioactivation of CCP are now known and have been approved. These consist of the following.

1. A *Bacillus mucilaginosus* culture based on an active strain from a selected collection grown on a selected nutrient medium is introduced directly into non-sterile clayey or clay-containing suspensions with definite moisture content and temperature and letting the suspension stand in a vessel with continual mixing for 3 to 30 days. Next, either a molding paste, from which casting slip is prepared, or press powder for pressing tiles is obtained [14, 15, 18].

2. The bacterial culture obtained from the most active strain separated directly from clayey raw material (kaolins, clays from local deposits, soils) is grown on a selected nutrient medium and introduced into non-sterile CCP as they are being prepared, after which the suspension is filtered and the molding paste is allowed to mature passively or the treated paste is used to obtain casting slip [22, 28].

3. A stable bacterial cenosis separated from clayey raw materials or clay-containing pastes and grown on a nutrient medium is introduced in a definite order into non-sterile clayey raw material and ceramic pastes. It was determined that in time the composition of the microorganisms changes from the initial composition of the microorganism in the clayey raw material and ceramic pastes to the higher content of anaerobic bacteria. When a bacterial cenosis is introduced the interaction between bacteria and natural microflora present in the clayey raw material is taken into account. Next, a ceramic paste is obtained by filtering and allowed to mature naturally for up to 30 days [16, 20].

4. Biotreatment of unsterile clayey raw material and ceramic pastes, whose moisture content is 50%, is effectuated by introducing a selected nutrient medium containing sources of carbon, nitrogen and phosphorus to ensure development of natural microflora in the raw material, represented by aerobic and anaerobic bacteria effectuating reduction, which promotes dissolution of iron compounds. The treated dispersion is kept for 10 – 35 days, dehydrated by decantation, washed with a solution of ammonium oxalate and undergoes magnetic separation [16].

5. Passive maturing of ceramic paste containing natural microflora in moist and warm enclosures, paste storage and charge stockrooms for subsequent molding by rollers or preparation of casting slip [2, 3].

A feature common to all the examples of biotreatment presented above is the introduction of the most active strains of bacteria into the clayey dispersions being treated or the activation of natural microflora present in clayey materials. The problem of improving the rheological properties of ceramic paste and casting slip was solved even though the bacteria are of different origin and their cultivation media are different as are the methods of activation of the microflora present in the raw materials with the addition of nutrient media and the creation of favorable conditions for the multiplication of the bacteria.

Role of the Culture Liquid Components and Nutrient Medium in the Biotreatment of CCP. Even though similar results were obtained using different methods of treatment, the mechanisms of processing and time periods sufficient to obtain the required results are not always identical. Thus, when *Bacillus mucilaginosus* nutrient medium is introduced into a ceramic suspension the properties of the medium come into play during the first few days: filterability decreases and the threshold and rate of structure formation increase [3]. Such a change occurring simultaneously in the values of the three indicators shows that the degree of aggregation of clayey particles decreases and the degree of dispersion of clayey minerals of the ceramic suspension increases with disaggregation being the predominate process. The destruction of aggregates of clayey particles is explained by the influence of exopolysaccharides of *Bacillus mucilaginosus*, one of the products of the culture liquid — a metabolite, exhibiting surface-activity, from the activity of these bacteria. When the nutrient medium is introduced into a similar ceramic suspension in the first few days its properties are similar to those of the control suspension. Its rheological properties start to change on the third day at the earliest [15]. At the same time it should be noted that for more prolonged action of the metabolic products of the bacterial community organic gluing substances, which cause disaggregated particles to adhere to one another, are formed in the CCP, and this improves the filtration of fluid pastes [15]. It has not been ruled out that the aggregated particles of CPP comprise centers of crystallization during high-temperature firing of ceramics.

A number of factors must be taken into account when microorganisms cultured on artificial media are introduced into CPP: the total number of cells and their physiological state, the transport of matter into the ambient medium of a cell and the interaction of cells with other microorganisms present in the object.

In this connection, it is the opinion of the authors that when analyzing the results of experimental studies of ceramic pastes with addition of *Bacillus mucilaginosus* culture liquid a number of abiotic and biotic processes occurring during the period of its technological preparation and maturing must be taken into account. *Bacillus mucilaginosus* culture liquid is known to be a complex mixture which includes the following: a) *Bacillus mucilaginosus* bacteria or complex bacteria; b) residues of unused components of the nutrient medium; c) metabolic products of the bacteria (exometabolites) [12, 15, 16, 18, 20]. When they are introduced into the ceramic paste the role and mechanisms by which each component acts are distinguished as follows. 1) On the one hand the bacteria or bacterial community must adapt to the change in the living conditions while on the other hand nutrition is paramount for all microorganisms introduced into the composition for natural microflora [8]. For this reason, all microorganisms are interrelated either via competition for the common substrates or via cooperation in the use of these substrates; but, usually, cooperation is observed. The rate of increase of the number of microorganisms depends on the concentration of the substrate; as it is consumed one nutrient substrate is replaced and the dominant forms change. The exometabolites of one organism serve as a nutrient substrate for another, and as a result trophic relations arise between microorganisms. 2) Most likely, the natural microflora utilized the unused components of the nutrient medium of the culture liquid, i.e., different functional groups of microorganisms undergo development. 3) Exometabolites of the culture liquid also fulfill different functions depending on their composition: some metabolites change the properties at the moment they are introduced into the ceramic paste — the pH and Eh of the dispersion medium decrease, the dispersion phase is modified (disaggregation of particles, peptization of clayey minerals, and so on), and other metabolites are nutrient substrates for individual forms of microorganisms [20]. For this reason, many authors note [15, 17, 20] that during the first few days of maturing of a ceramic paste with a bio-additive, and depending on its concentration, the redox state of the dispersion changes from oxidative or weakly reducing to reducing or strongly reducing. Therefore, the compositional structure of a cenosis of microorganisms changes from predominantly aerobic to strictly anaerobic.

Similar results are obtained after the ceramic pastes into which nutrient substances or *Bacillus mucilaginosus* nutrient medium are introduced mature: the optimal molding moisture content and yield stress decrease, the post-drying strength and apparent density of the samples increase, and the sintering processes and the properties of the ceramic improve [3].

Nature and Mechanisms of Biological and Biochemical Processes during Biotreatment of CCP. The regularity of the breakdown of the minerals in ceramic paste and the mechanism of these processes are determined largely by the nature of the minerals and microorganisms and the exometabolites acting on the minerals.

A number of the processes of structural disordering, recrystallization, dissolution and synthesis of minerals in a CPP occur with the participation of biota and organic substances. The main difference of abiotic from biological and biochemical breakdown of the crystal structure of minerals is that the attainment methods and the mechanisms of these reactions are fundamentally different.

It is now known that diverse forms and combinations of microorganisms act on the same mineral by different mechanisms [1, 7, 8, 28, 29]. Their activity can be indirectly or directly responsible for the breakdown of minerals and the transition of the constituent elements of minerals into a mobile state. In the case of indirect action of microorganisms on minerals, the problem is one of breakdown by the metabolites produced by microorganisms and comprising chemical reagents — organic and mineral acids, chelating agents and reducing substances. However, neither the organic compounds participating in these processes nor the mechanism by which minerals dissolve has yet been established. It is unclear whether the specific dissolving power of simple organic and mineral acids plays a part or the process is due to the participation of high-molecular compounds that effectuate quite complex mechanisms, possibly, fermentative, or organic substances effectuate electrochemical processes: an organic substance participates as an electron donor – a source of energy (it oxidizes) and as an electron carrier from Fe-reducing bacteria to Fe(III) (electronic shuttle [29 – 31].

Some investigators attach great importance to the breakdown of minerals by organic acids of microbic origin. The most commonly formed organic acids are oxalic, acetic, gluconic and other acids. Almost all organic acids transform, in one way or another, crystalline minerals into the amorphous state. It has been noted that the actions of organic acids on minerals are more diverse than that inorganic acids, since it depends on combinations of the functional groups in their molecules. The intensity of breakdown of minerals by acids is explained by the fact that among the acids produced by microorganisms there are many compounds which possess simultaneously not only the properties of acids but also the capability to form complex compounds. The enormous role which complexation plays in breakdown of low-solubility minerals is now generally recognized [1, 7].

Other investigators single out mechanisms by which microorganisms act directly on minerals containing elements with variable valence, predominately ferruginous elements [1, 16, 17, 20, 25, 29 – 31]. It is well known that heterotrophic microorganisms falling into anaerobic living conditions use Fe(III) instead of oxygen for respiration [8].

A network of interconnected chemical reactions is formed in the trophic chain of a microbial community.

Groups of microorganisms obtain energy for vital activity from redox reactions, which comprise electron transfer from donor to acceptor. Essentially, a system of electrochemical reactions exists in the energetics of microorganisms. According to Lovley's scheme [31], organic substances fall into two classes [31]:

1) an organic substance as a source of energy, i.e., as an electron donor; sugar, acetate, and lactate are used in experiments on supplying energy;

2) an organic acid as an electron carrier from reducing bacteria to Fe(III).

In mineral rocks and soils it is mainly humic acids that act as electron carriers [29]. In contrast to organic matter in the first group the electronic shuttle is not consumed in the Fe(III) reduction process. All iron-reducing bacteria, including the model bacteria *Geobacter metallireducens* and *Shewanella alga*, are capable of using humic acids and their analogs as the only electron acceptor in the biological oxidation of acetate, lactate, or hydrogen. Microorganisms effectuating fermentation as well as sulfate reducers and methanogens have the same capability. Reduced humic acids are capable of carrying electrons to Fe(III) as a result of a chemical reaction, forming Fe(II) and regenerating the oxidized form of humic acids. In other words, humic acids act as an exogenic electron shuttle and can carry electrons repeatedly to (hydr)oxides.

Practical Experience in Biotreatment of Ceramic Pastes. In order for industry to adopt the biotreatment of ceramic pastes it is important that biosuspensions be easy to prepare and easy to introduce into the clay-containing dispersions being treated. Biotechnology for treating ceramic pastes was first adopted on commercial and semi-commercial scales at the beginning of the 1990s at the Minsk Building Materials Combine (Republic of Belarus) and Dmitrov Porcelain Works (Farfor Verbilok, JSC). The BIOTON project, which the Ministry of Education and Science finances, is being implemented in Germany. The objective of these works was to apply biotreatment of the clayey materials used in the ceramic industry [32]. The results obtained in the process of adopting biotreatment of ceramic pastes have confirmed that biotreatment is effective and that microflora play a functional role in pastes. In the industrial use of biotreatment for different pastes (production of tiles, domestic porcelain) the rheological properties of suspensions and ceramic pastes and the sintering temperature of ceramic articles changed considerably, the shrinkage in the air-dry state decreased and the mechanical strength of the intermediate product and articles increased. For domestic porcelain, the amount of technological wastes decreased, equipment productivity increased, and the whiteness of articles increased.

The conventional method of improving the technological properties of porcelain paste by means of passive maturing in paste storage facilities has been used thus far in a number of ceramic plants abroad and in the Russian Federation. For example, the maturing technology for porcelain paste after the first kneading in paste storage at controlled temperatures and moisture content was used at the porcelain plant KPM in the Federal Republic of Germany (König Porcelain Manufacture, Berlin). It has been determined that the quality of ceramic paste and finished articles improved considerably: the plasticity of paste, mechanical strength, cracking resistance of the intermediate product and the whiteness of articles increased while the amount of technical wastes decreased. Passive maturing of molding porcelain paste with moisture content 23 – 25% at temperature 18 – 22°C (unregulated conditions) for one or more months for the production of thin-walled articles was used at Farfor Verbilok, JSC (previously the Dmitrovskii Porcelain Works). According to observations made by specialists at the plant over a period of many years, for passive maturing the formation rate of the casting and the mechanical strength of the intermediate product as well as the impact toughness and whiteness of articles increase while the number of defects on finished articles decreases.

REFERENCES

1. G. I. Karavaiko, "Microbial destruction of silicate minerals," in: *Proceedings of the S. N. Vinogradskii Institute of Microbiology* [in Russian], Nauka, Moscow (2004), Issue 12, pp. 172 – 196.
2. A. I. Avgustinik, *Ceramics* [in Russian], Stroiizdat, Moscow (1975).
3. G. N. Maslennikova, Yu. T. Platov, R. A. Khalilullova, et al., "Effect of microorganisms on the properties of porcelain pastes during maturing (review)," *Steklo Keram.*, No. 10, 15 – 23 (1999); G. N. Maslennikova, Yu. T. Platov, R. A. Khalilullova, et al., "Effect of microorganisms on the properties of porcelain mixtures in maturing (review)," *Glass Ceram.*, **56**(9 – 10), 312 – 319 (1999).
4. P. P. Budnikov, *Ceramic Technology: Raw Materials for Ceramic Production, Methods for Studying and Processing Them* [in Russian], GNTI Ukraine, Khar'kov – Kiev (1937).
5. V. A. Kind and S. D. Okorokov, *Building Materials: Production, Properties and Application* [in Russian], Gosstroiizdat, Leningrad – Moscow (1934).
6. M. M. Bogachikhin, *Ceramics in China: History, Legends Secrets* [in Russian], Fast-Print, Moscow (1998).
7. T. V. Aristovskaya, *Microbiology of Soil-Formation Processes* [in Russian], Nauka, Moscow (1980).
8. G. A. Zavarzin and N. N. Kolotilova, *Introduction to the Natural Science of Microbiology* [in Russian], Universitet, Moscow (2001).
9. M. F. Hochella, "Sustaining Earth: Thoughts on the present and future role of mineralogy in environmental science," *Miner. Mag.*, **66**, 627 – 652 (2002).
10. V. G. Aleksandrov and G. A. Zak, "Bacteria breaking down aluminum silicates," *Mikrobiologiya*, **19**(2), 97 (1950).
11. Z. A. Avakyan, T. A. Pivovarova, and G. I. Karavaiko, "Characteristics of a new form Bacillus mucilaginosus," *Mikrobiologiya*, **55**(3), 477 – 482 (1986).
12. K. I. Surman, *On Soil Bacteria Resembling Bacillus mucilaginosus, Author's Abstract of Candidate's Thesis* [in Russian], Leningrad (1962).
13. A. S. Vlasov, "Biological methods of enriching mineral raw materials and technological mixtures in the production of ceramics," in: *Chemistry and Technology of Silicate and Heat-Re-*

sistant Non-Metal Materials [in Russian], Leningrad (1989), pp. 155 – 165.
14. V. V. Baranov, *Effect of Biotreatment of Ceramic Pastes on the Technology and Properties of Ceramic Facing Tile, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1985).
15. A. N. Chernyshev, *Effect of Biotreatment of Pastes on the Technological Properties of Porcelain, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1990).
16. R. A. Khalilullova, *Increasing the Whiteness of Porcelain by Complex Treatment of Mineral Raw Material, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1994).
17. R. A. Platova and G. N. Maslennikova, "Biochemical nature of the gley formation during maturing of clayey materials," *Steklo Keram.*, No. 9, 14 – 20 (2009); R. A. Platova and G. N. Maslennikova, "Biochemical nature of the gley formation during aging of clayey materials (reviews)," *Glass Ceram.*, **66**(9 – 10), 318 – 323 (2009).
18. E. M. Dyatlova, E. S. Kakoshko, V. A. Biryuk, and R. M. Markevich, "Improvement of rheological properties of clayey suspensions, treated by *Bacillus mucilaginosus* culture liquid," *Steklo Keram.*, **67**, No. 3, 29 – 32 (2010); E. M. Dyatlova, E. S. Kakoshko, V. A. Biryuk, and R. M. Markevich, "Improvement of the rheological properties of clayey suspensions, treated with *Bacillus mucilaginosus* culture liquid," *Glass Ceram.*, **67**(3 – 4), 89 – 92 (2010).
19. Z. A. Avakyan, Yu. T. Platov, R. A. Khalilullova, G. N. Maslennikova, et al., *Method of Whitening Clay-Containing Ceramic Raw Material, RF Patent No. 2083527, July 10, 1997* [in Russian]; application No. 95116993.
20. E. S. Turova, *Microbial Transformation of Kaolins and Kaolin-Containing Raw Material, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1997).
21. E. S. Shelobolina, S. M. Pickering, and D. R. Lovley, "Fe-cycle bacteria from industrial clays mined in Georgia, USA," *Clay and Clay Minerals*, **53**(6), 580 – 586 (2005).
22. I. Styriakova and I. Styriak, "Iron removal from kaolins by bacterial leaching," *Ceramics – Silicate*, **44**(4), 135 – 141 (2000).
23. Hailiang Dong, Deb. P. Jaisi, and J. Kim, "Microbe – clay mineral interactions," *Am. Mineralogist*, **94**(11 – 12), 1505 – 1519 (2009).
24. M. R. Hosseini, M. Pazouki, and M. Ranjbar, "Bioleaching of iron from highly contaminated kaolin clay by Aspergillus niger," *Applied Clay Sci.*, **37**(3 – 4), 251 – 257 (2007).
25. Volkan Arslan and Oktay Bayat, "Removal of Fe from kaolin by chemical leaching and bioleaching," *Clay and Ñlay Minerals*, **57**(6), 787 – 794 (2009).
26. Min-Rong Guo, Qiu-Xiang He, and Yu-Man Li, "Removal of Fe from kaolin using dissimulator Fe(III)-reducing bacteria," *Clay and Clay Minerals*, **58**(4), 515 – 521 (2010).
27. Anandita Roy, Samarendra K. Singh, and P. C. Banerjee, "Biobeneficiation of kaolin and feldspar and its effect on fired characteristics of triaxial porcelain," *Bull. Mater. Sci.*, **33**(3), 333 – 338 (2010).
28. J. Rossi, "Biodegradation of alumino-silicates: advances and perspectives," in: *Proc. Intern. Seminar on Biotechnology of Metals* [in Russian], Moscow (1985), pp. 412 – 424.
29. Yu. N. Vodyanitskii, *Chemistry, Mineralogy and Color of Gleyed Soils* [in Russian], GNU Pochvennyi institute, Moscow (2006).
30. E. E. Roden, "Analysis of long-term bacterial vs. chemical Fe(III) oxide reduction kinetics," *Geochimica et Cosmochimica Acta*, **68**(15), 3205 – 3216 (2004).
31. D. R. Lovley, "Extracellular electron transfer: wires, capacitors, iron lungs, and more," *Geobiology*, No. 6, 225 – 231 (2008).
32. K. Emmerich and R. Schuhmann, "Comprehensive material characterization of clay mineral raw material for the development of microbiological processing technologies," *cfi/Ber.DKG*, **86**(3), 29 – 34 (2009).